



## Proton Conductivity of Refractory Metal Phosphates at Intermediate Temperatures

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# Proton Conductivity of Refractory Metal Phosphates at Intermediate Temperatures

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# Outlines

## Introduction

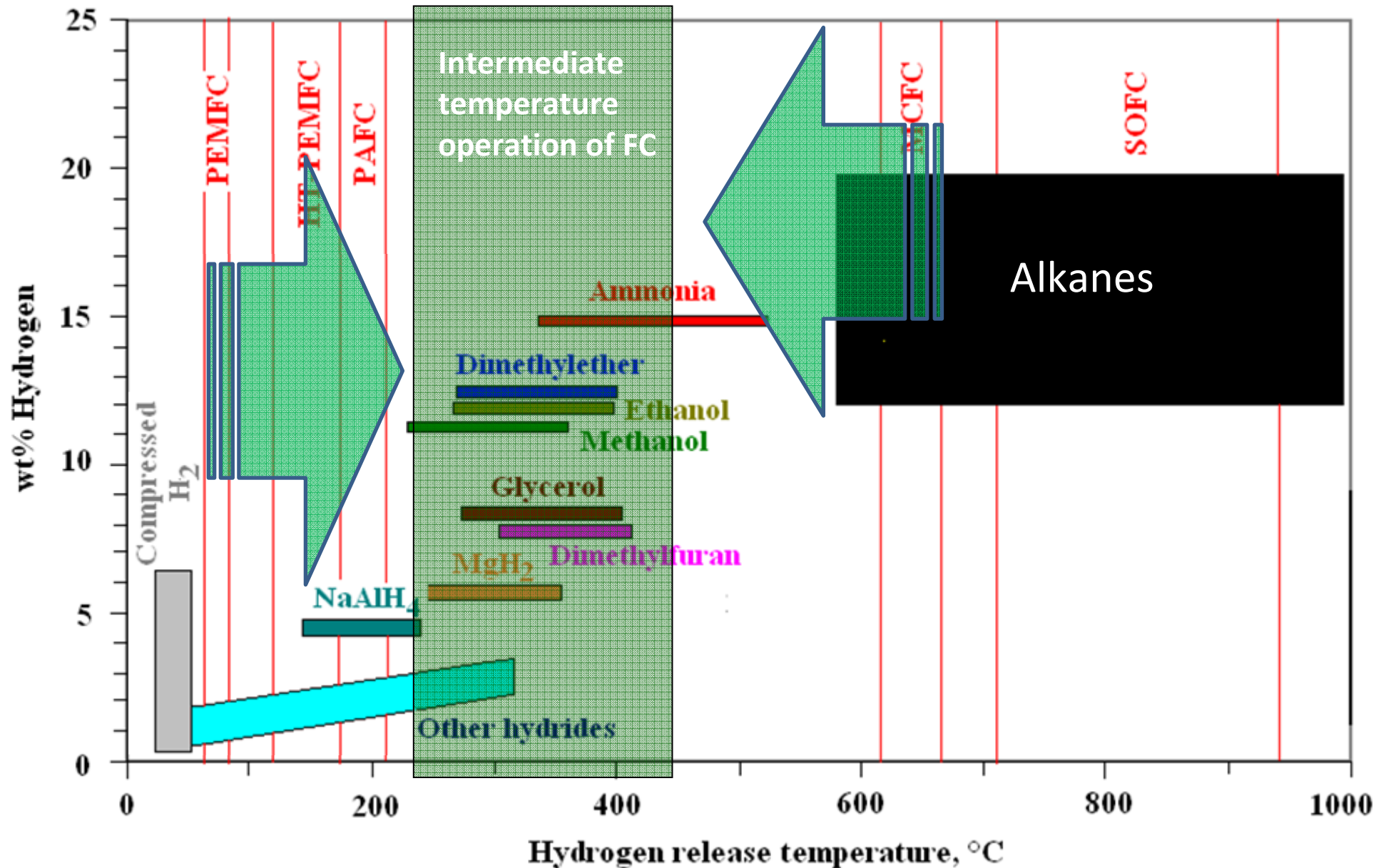
- Refractory metals and their phosphates

## Niobium phosphates

- Anhydrous Conductivity
- Heat Treatment Temperature
- Crystalline forms
- Indium doping
- Morphology effects – sol-gel method
- Further stability evaluation
- OCV & EMF

## Conclusions

# Intermediate temperature operation - and fuelling of fuel cells



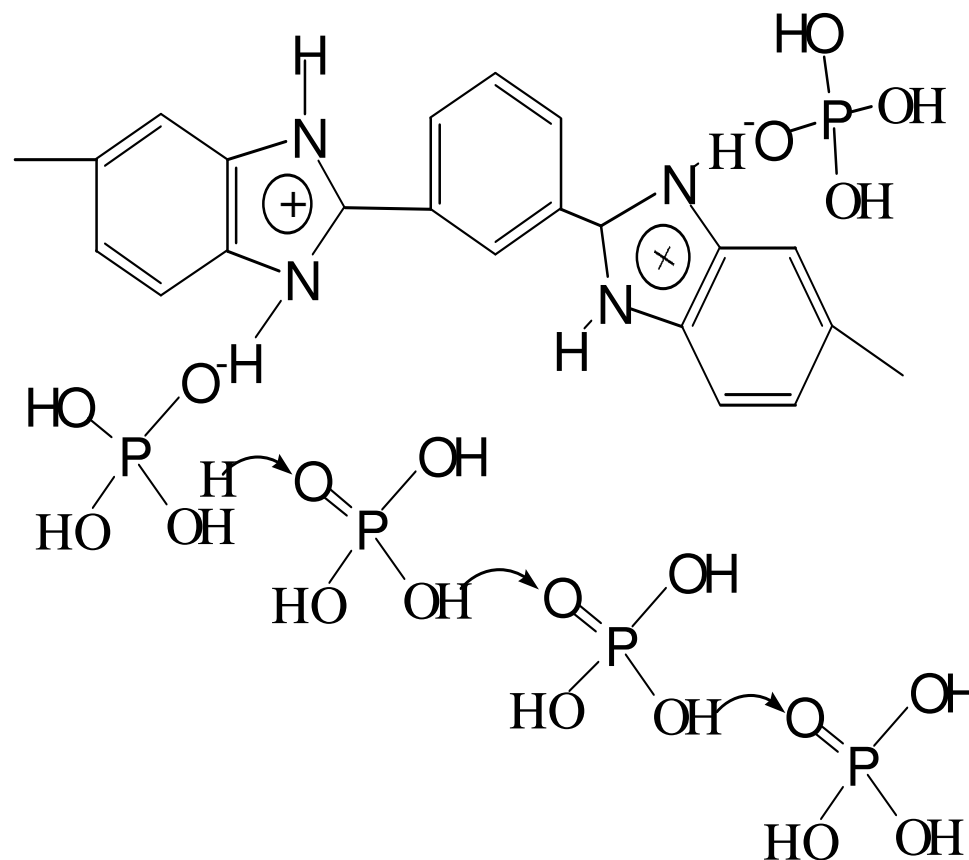
# PBI/PA Conductivity

## $\text{H}_3\text{PO}_4$ Protonates PBI

- **IR measurements indicate max protonation at  $n=2$**
- Very low conductivity with  $n < 2$  indicating little N-H to N-H proton hopping
- **$\text{H}_2\text{PO}_4^-$  predominates over concentration range ( $n=6$ )**
- Low activation volume measured
- **$t_{\text{H}^+}$  measured  $\sim .98$  for  $n=6$**
- Activation energy consistent with Grotthuss mechanism

## Above 200°C

- **Acid condensation**
- **Acid evaporation**
- **Polymer degradation**
- .....



# Refractory metal oxides

Vanadium, Niobium, Tantalum.....

- High surface acidity
  - Lewis acid sites  $\text{Me}=\text{O}$
  - Brønsted acid sites  $\text{Me}-\text{OH}$
- Solid acid catalysts for reactions such as
  - esterification
  - polycondensation
  - dehydration
- ÷ Significantly decreased acidity at elevated temperatures  
(below 700 K)

## Refractory metal phosphates

- Phosphoric acid treated oxides
- Further increased surface acidity
  - both  $\text{Me}-\text{OH}$  and  $\text{P}-\text{OH}$
- Acidity preserved at elevated temperatures
  - due to formation of polyphosphates



# Vanadium & niobium phosphates

Layered structure



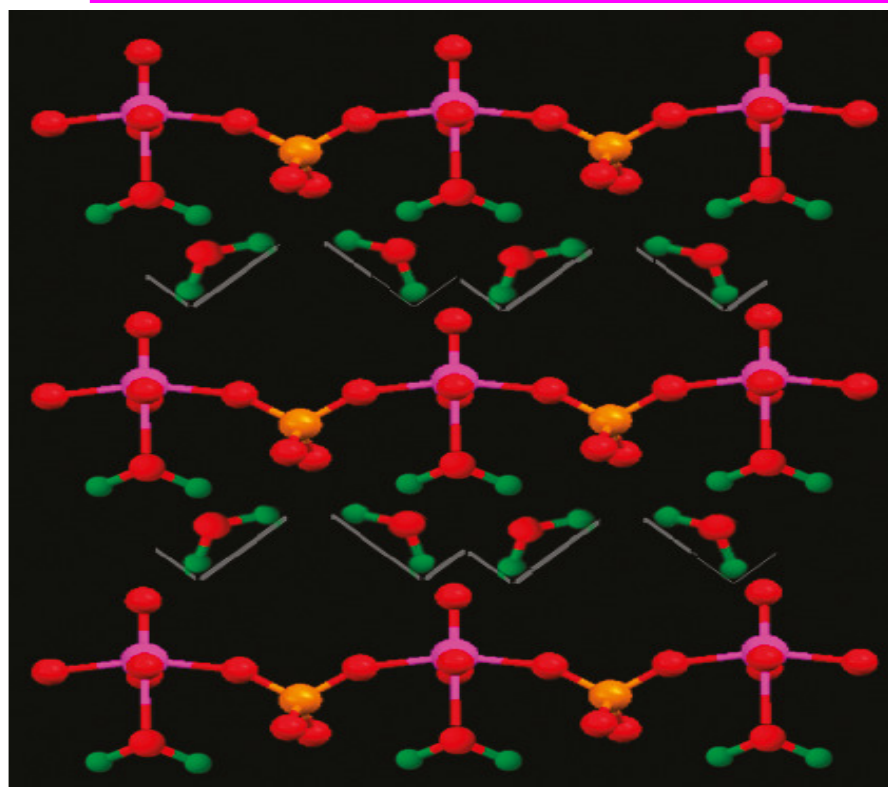
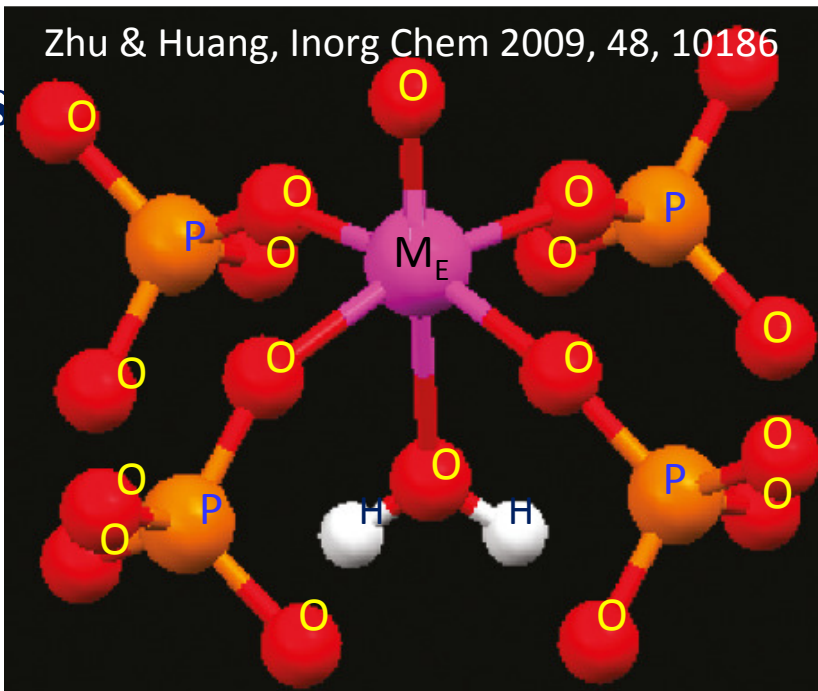
$\text{M}_\text{E}\text{O}_6$  octahedra

connected to four  $\text{PO}_4$  tetrahedra

one axial group  $\text{M}_\text{E}=\text{O}$

other axial ligands ( $\text{H}_2\text{O}$ )

Zhu & Huang, Inorg Chem 2009, 48, 10186



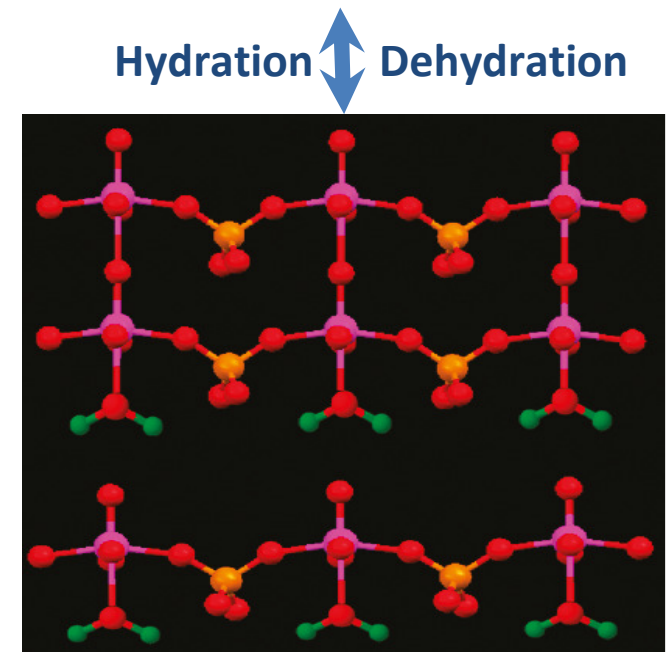
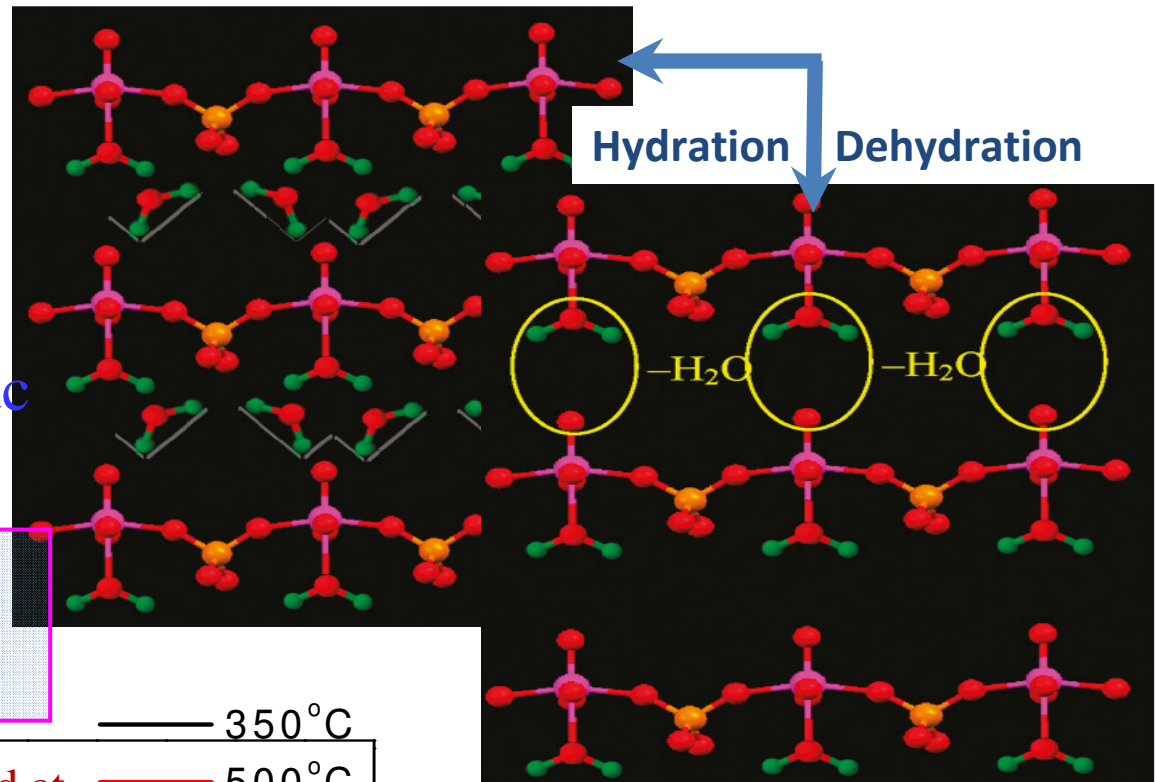
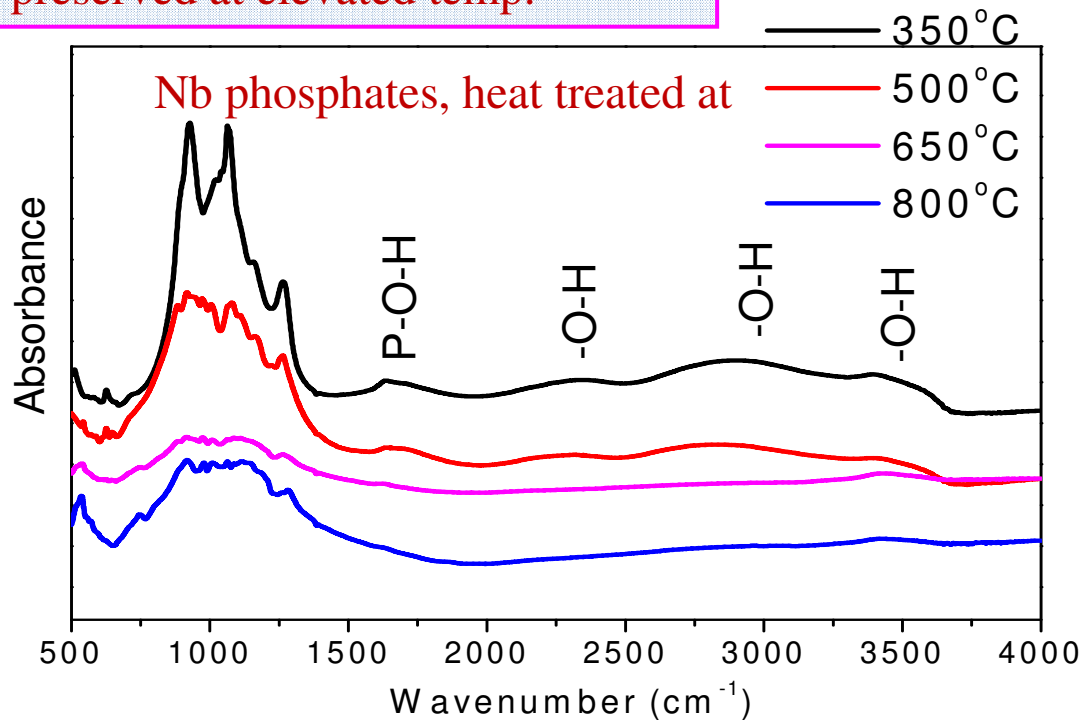
- With both Lewis and Brønsted acid sites
  - strong acidity and catalytic activities towards acid-catalyzed reactions
- Layered/3-dimension structures
  - intercalation capacity of the interlamellar space
    - ammonia, amines, alcohols
    - acid molecules  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{SO}_4$ , etc
  - strong hydrogen bonding involved

# Nb phosphates

and Vanadium phosphates

- up to 5 H<sub>2</sub>O molecules
- dehydration at HT led to P-O-P/Nb-O-P bonds
- reversible hydr./dehydr.

Both Nb-OH and P-OH  
preserved at elevated temp.

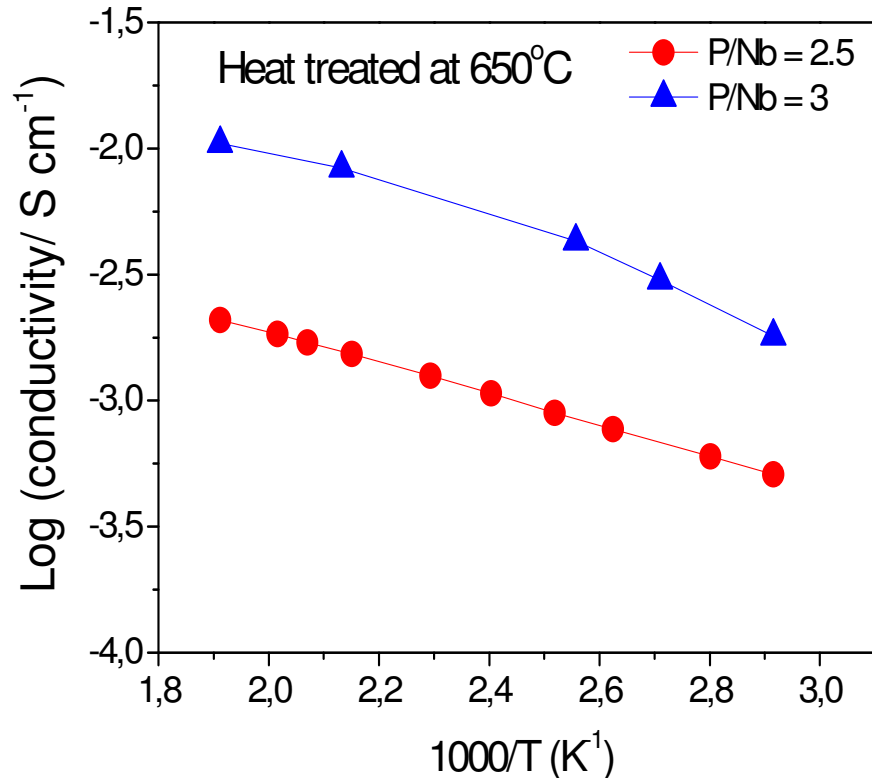




# Anhydrous Conductivity and water vapor dependence

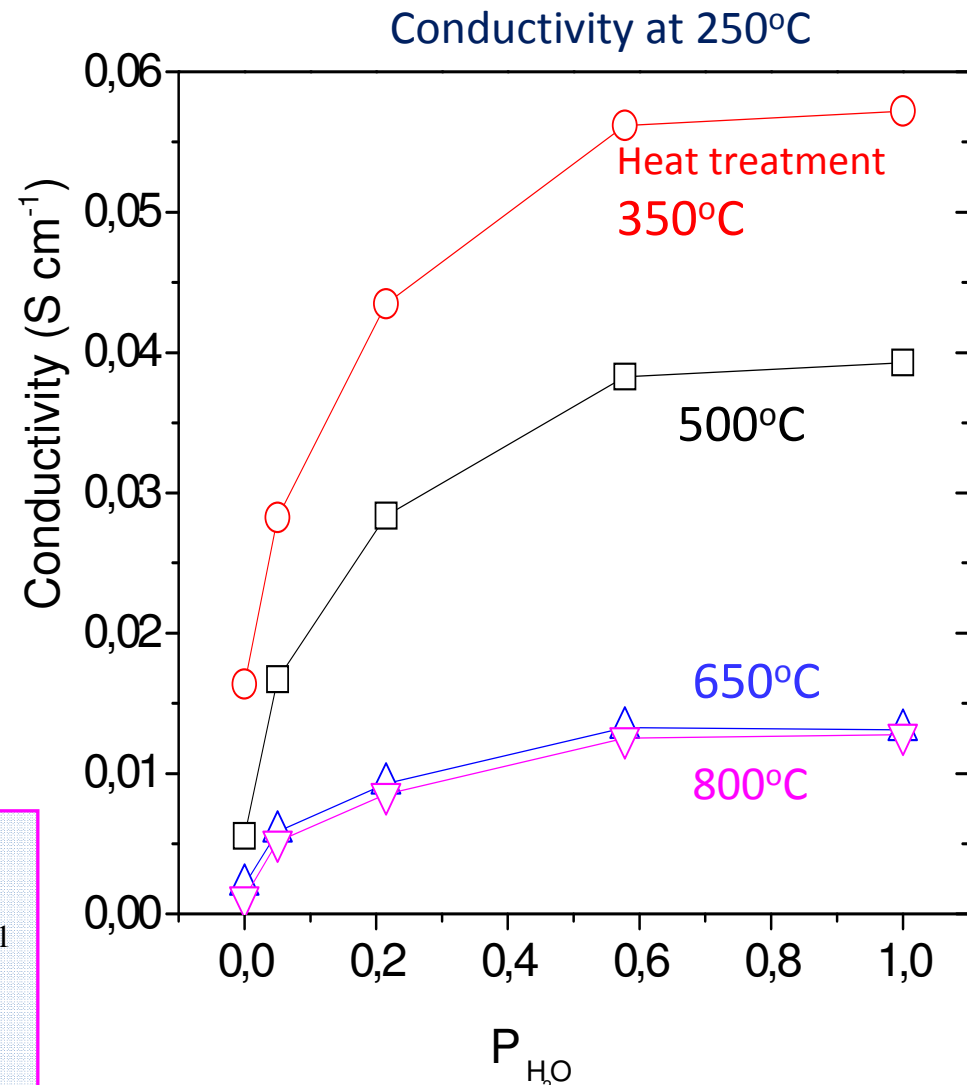
Strong dependence

- on heat treatment temperature
- on atmospheric humidity



## Anhydrous conductivity

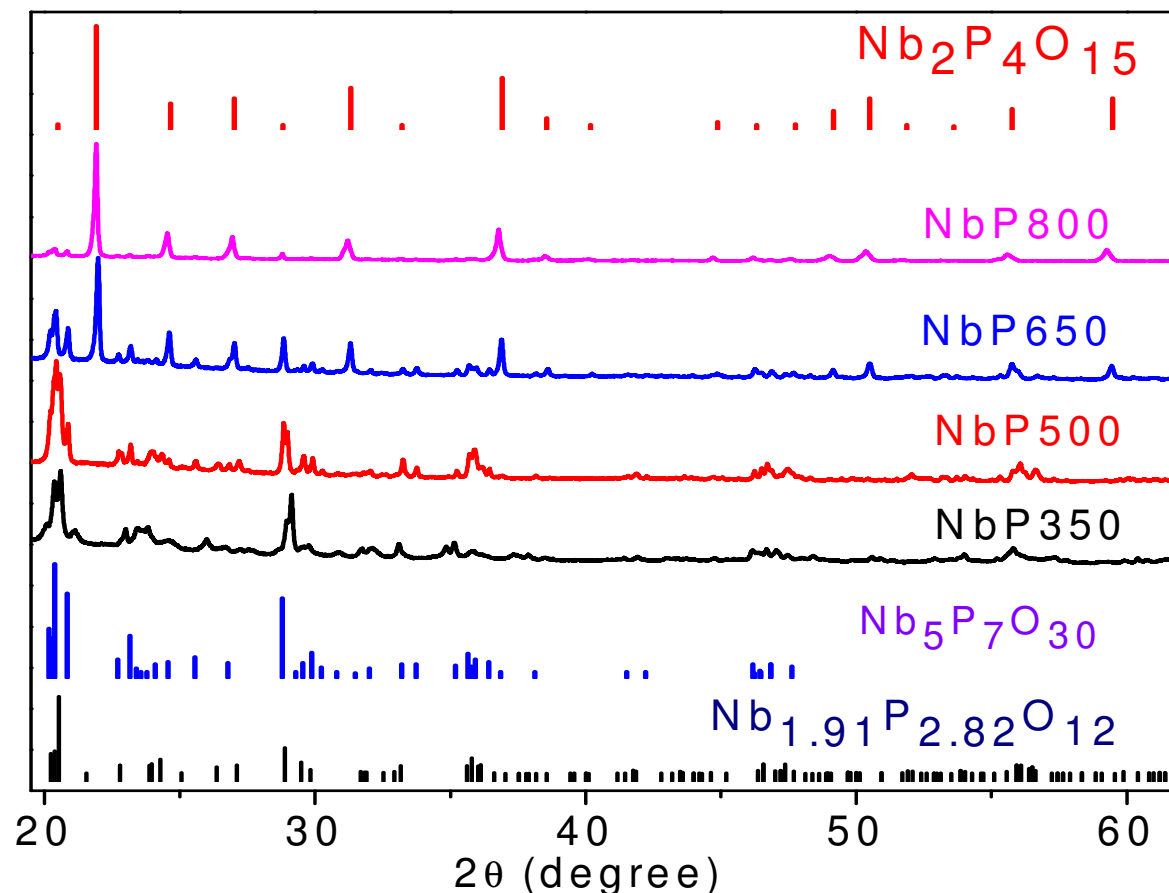
with an activation energy of 16-24 kJ mol<sup>-1</sup>  
- typical for the Grotthuss mechanism of  
proton migration in condensed phases



# Heat Treatment Temperature

- phosphate structures

P/Nb = 2.0



Synthesis	
Initial molar ratio P/Nb	Heat treatment temperature (°C)
P/Nb = 4.0	650
P/Nb = 3.0	350 500 650 800
P/Nb = 2.5	350 500 650 800
P/Nb = 2.0	350 500 650 800

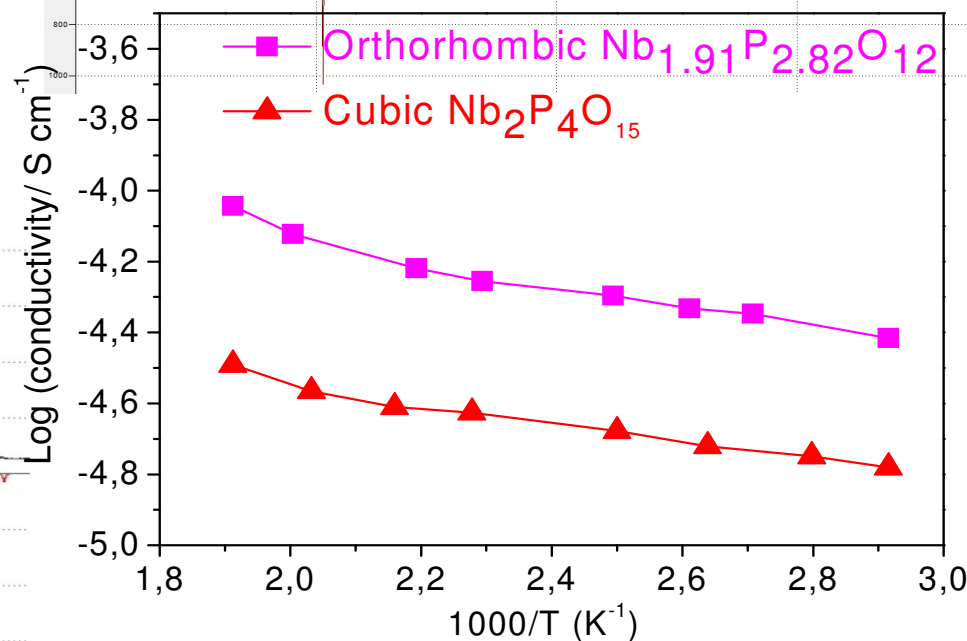
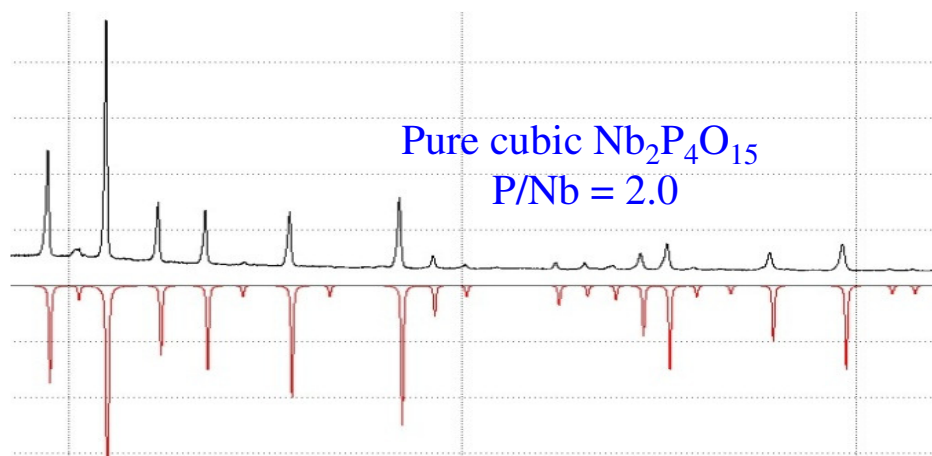
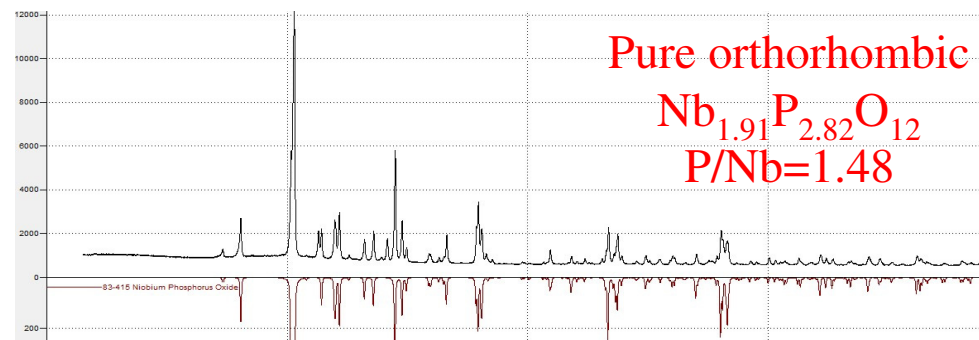
	Theoretic. density, g/cm <sup>3</sup>	Crystal parameters of unit cell						Notes
		a	b	c	$\alpha$	$\beta$	$\gamma$	
Monoclinic $\text{Nb}_5\text{P}_7\text{O}_{30}$	3,37	29.8	8,7	8,8	90	91.8	90	Favors at LT
Cubic $\text{Nb}_2\text{P}_4\text{O}_{15}$	3.15	8,0	8,0	8,0	90	90	90	Favors at HT
Orthorhombic $\text{Nb}_{1.91}\text{P}_{2.82}\text{O}_{12}$	3,31	12.1	8,7	8,7	90	90	90	Minor phase <sup>9</sup> Favors at LT

# Crystalline forms

- Orthorhombic  $\text{Nb}_{1.91}\text{P}_{2.82}\text{O}_{12}$
- Cubic  $\text{Nb}_2\text{P}_4\text{O}_{15}$

## Anhydrous conductivity

- Orthorhombic  $\text{Nb}_{1.91}\text{P}_{2.82}\text{O}_{12}$ 
  - higher anhydrous conductivity in the whole temperature range

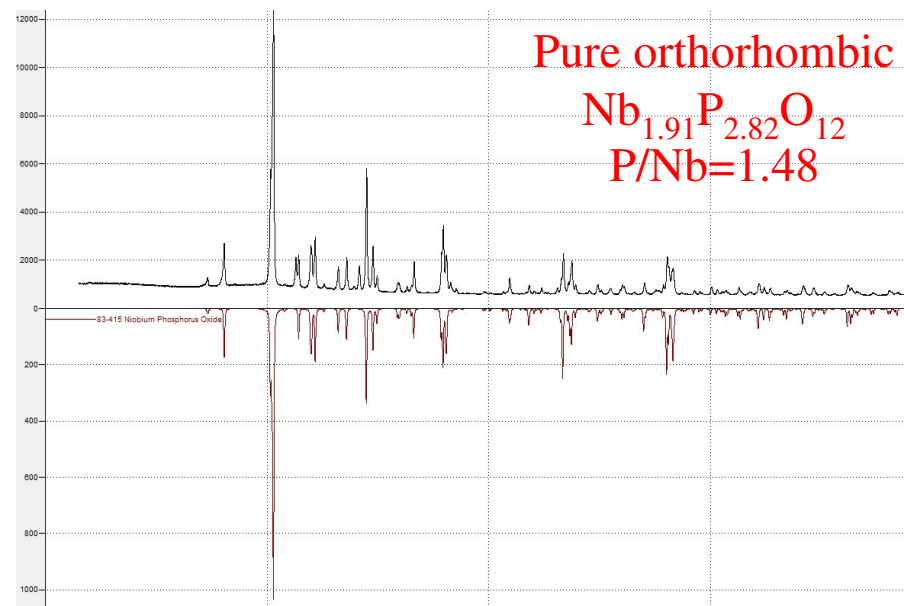
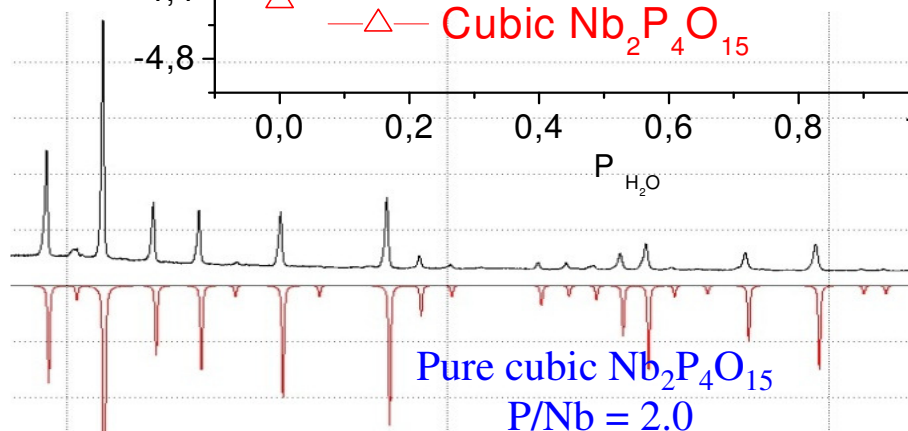
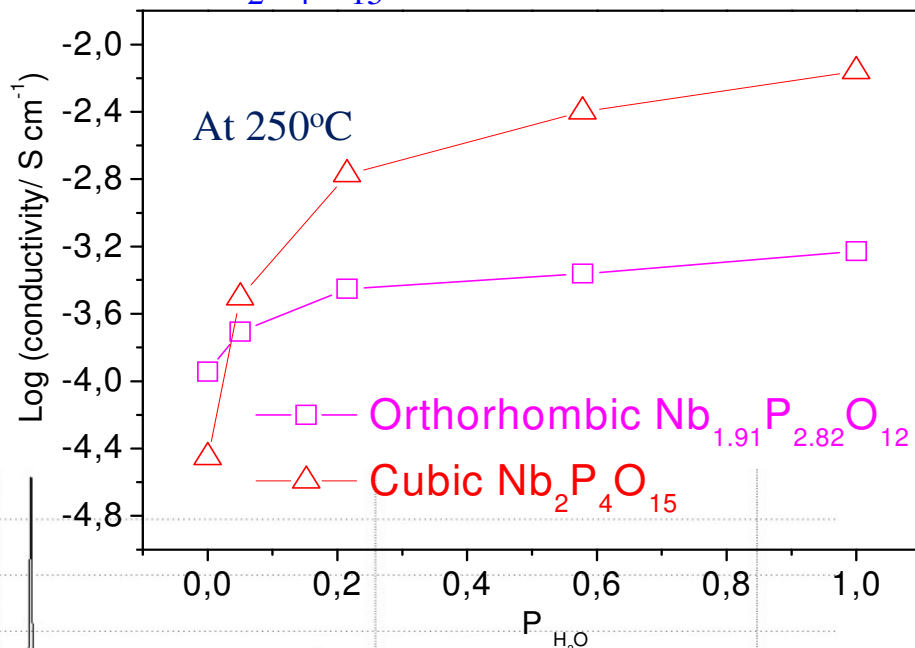


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Cubic $\text{Nb}_2\text{P}_4\text{O}_{15}$	3.15	8,0	8,0	8,0	90	90	90	Favors at HT
Orthorhombic $\text{Nb}_{1.91}\text{P}_{2.82}\text{O}_{12}$	3,31	12.1	8,7	8,7	90	90	90	Minor phase Favors at LT

# Crystalline forms

- Orthorhombic  $\text{Nb}_{1.91}\text{P}_{2.82}\text{O}_{12}$

- Cubic  $\text{Nb}_2\text{P}_4\text{O}_{15}$



## Dependence of conductivity on $\text{P}_{\text{H}_2\text{O}}$

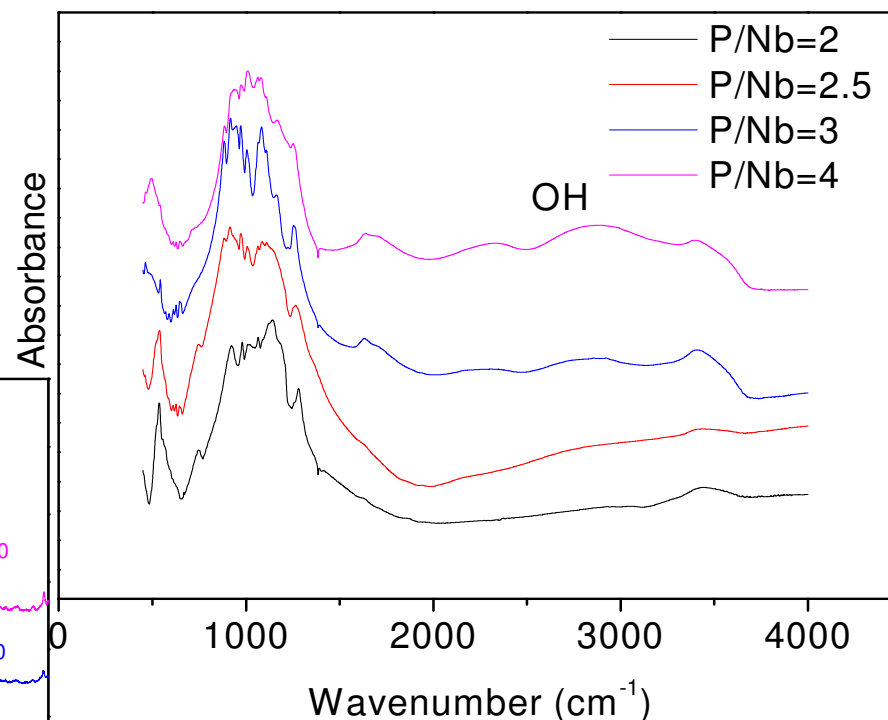
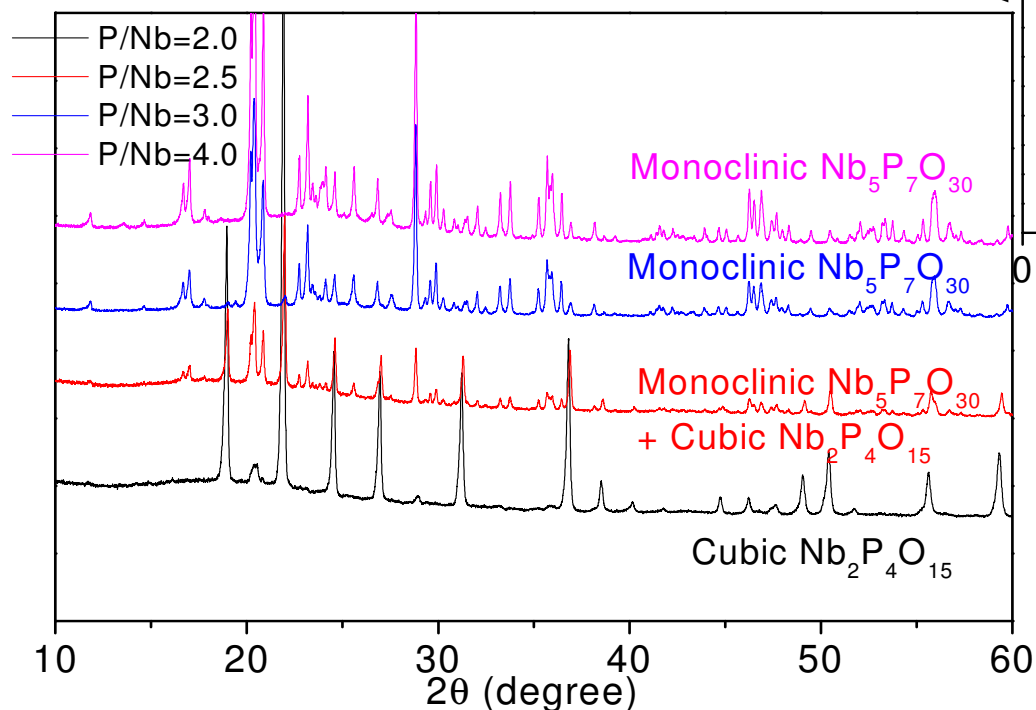
- Cubic  $\text{Nb}_2\text{P}_4\text{O}_{15}$  stronger dependence
- higher conductivity at higher  $\text{P}_{\text{H}_2\text{O}}$

	Theoretic. density, g/cm <sup>3</sup>	Crystal parameters of unit cell						Notes
		a	b	c	$\alpha$	$\beta$	$\gamma$	
Monoclinic $\text{Nb}_5\text{P}_7\text{O}_{30}$	3,37	29.8	8,7	8,8	90	91.8	90	Favors at LT
Cubic $\text{Nb}_2\text{P}_4\text{O}_{15}$	3.15	8,0	8,0	8,0	90	90	90	Favors at HT
Orthorhombic $\text{Nb}_{1.91}\text{P}_{2.82}\text{O}_{12}$	3,31	12.1	8,7	8,7	90	90	90	Minor phase Favors at LT

# P/Nb Ratios

XRD – heat treatment at 650°C:

- P/Nb = 2.0: Cubic
- 2.5: Cubic + monoclinic
- 3-4: monoclinic



FTIR – heat treatment at 650°C

- P/Nb = 2.0: Low OH concentration
- 2.5-4.0: higher OH content

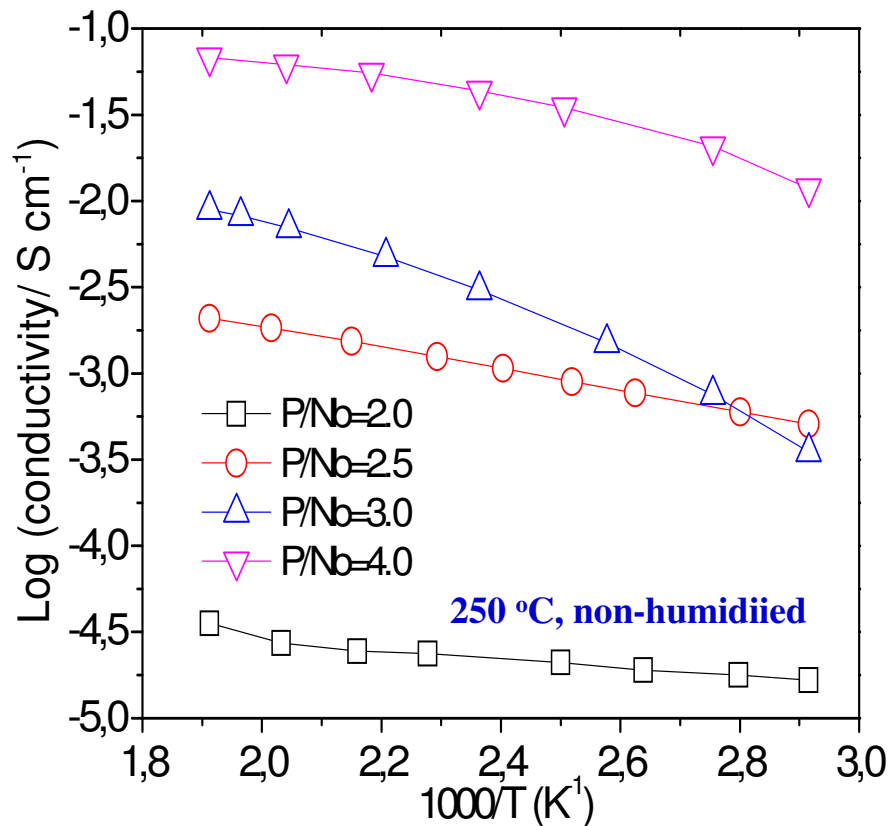
	Theoretic. density, g/cm <sup>3</sup>	Crystal parameters of unit cell						Notes
		a	b	c	α	β	γ	
Monoclinic Nb <sub>5</sub> P <sub>7</sub> O <sub>30</sub>	3,37	29.8	8,7	8,8	90	91.8	90	Favors at LT, high P/Nb
Cubic Nb <sub>2</sub> P <sub>4</sub> O <sub>15</sub>	3.15	8,0	8,0	8,0	90	90	90	Favors at HT, low P/Nb
Orthorhombic Nb <sub>1,91</sub> P <sub>2,82</sub> O <sub>12</sub>	3,31	12.1	8,7	8,7	90	90	90	Minor phase, 12 Favors at LT



# P/Nb Ratios

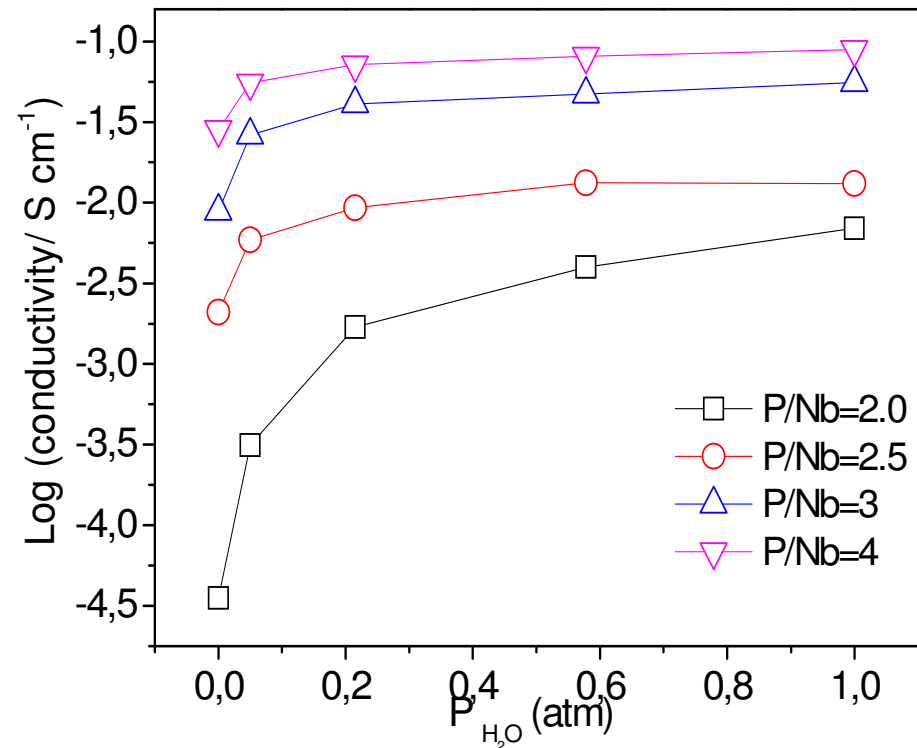
## XRD & FTIR

- P/Nb = 2.0: Cubic while low OH content
- 2.5: Cubic + monoclinic
- 3-4: monoclinic but high OH content



### Anhydrous conductivity

- P/Nb= 4: High - Monoclinic + high OH (amorphorous P<sub>m</sub>O<sub>n</sub> phase?)
- P/Nb= 2: Low - Cubic + Low OH



### Water vapor dependence

- P/Nb= 4: Less - Monoclinic + high OH (amorphorous P<sub>m</sub>O<sub>n</sub> phase?)
- P/Nb= 2: More - Cubic + Low OH

# Indium doping

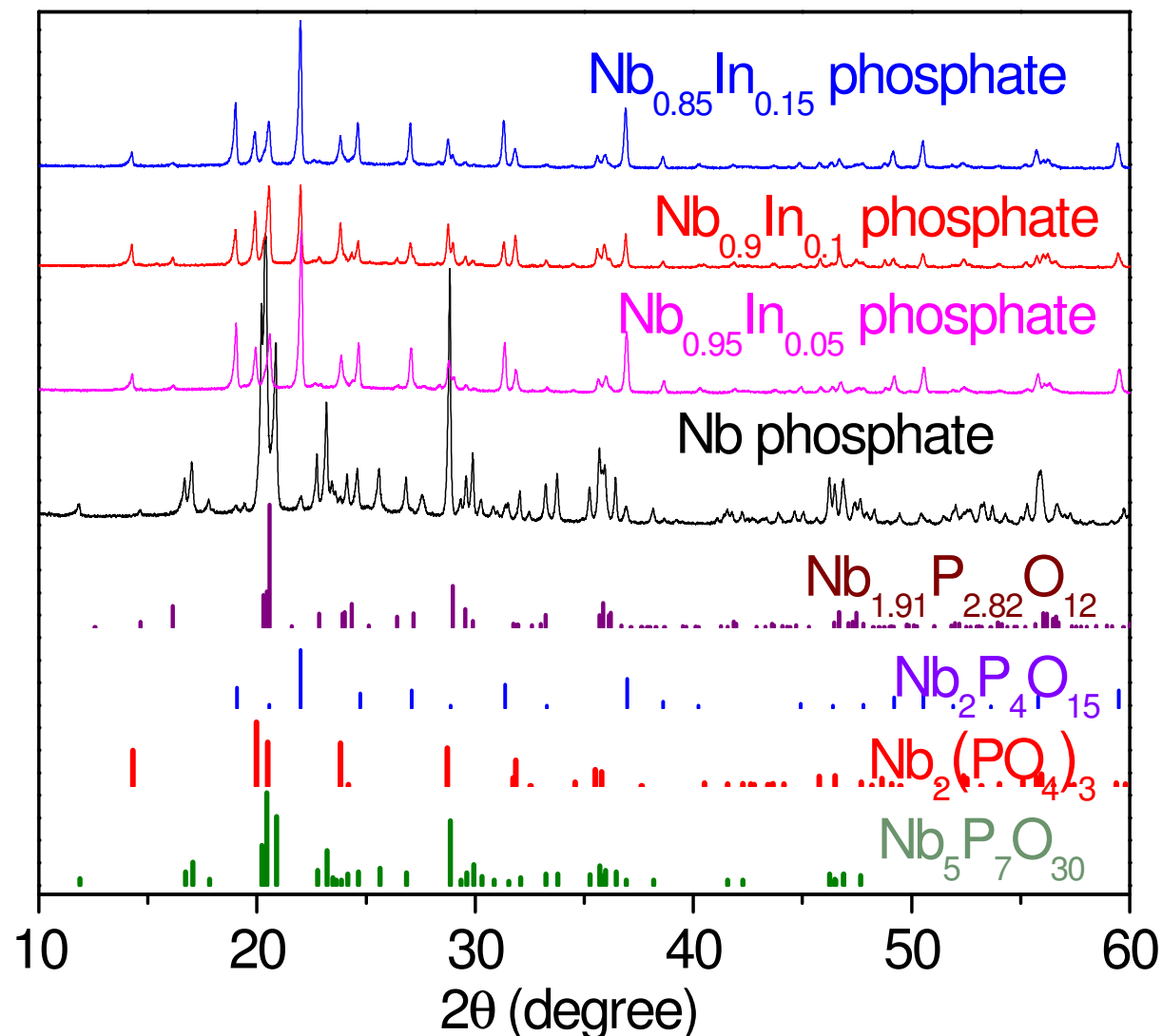
P/Nb = 3.0; 650°C

Pristine NbP:

Monoclinic Nb<sub>5</sub>P<sub>7</sub>O<sub>30</sub>

Indium doped NbP:

Cubic Nb<sub>2</sub>P<sub>4</sub>O<sub>15</sub>

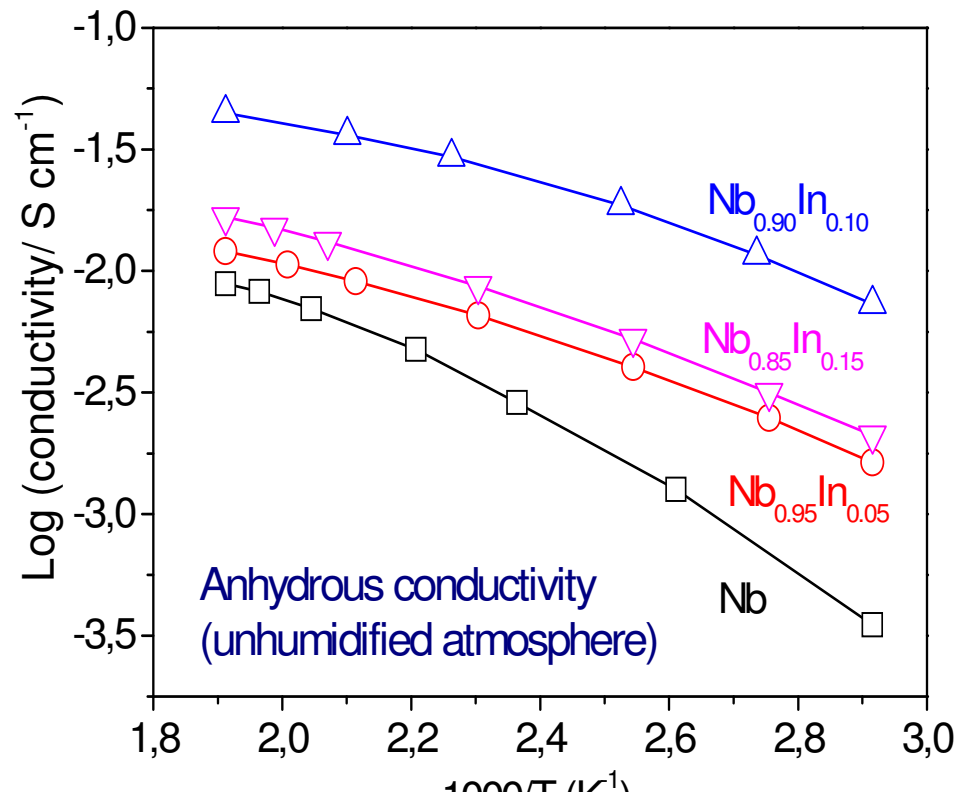
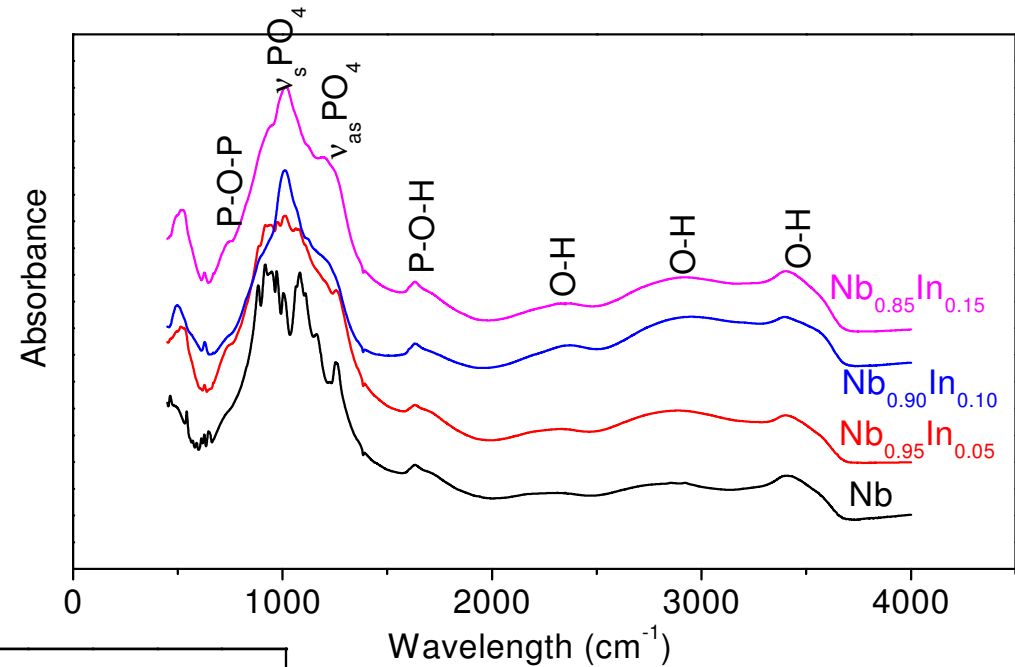


	Theoretic. density, g/cm <sup>3</sup>	Crystal parameters of unit cell						Notes
		a	b	c	α	β	γ	
Monoclinic Nb <sub>5</sub> P <sub>7</sub> O <sub>30</sub>	3.37	29.8	8,7	8,8	90	91.8	90	Favors at LT, high P/Nb; NbP
Cubic Nb <sub>2</sub> P <sub>4</sub> O <sub>15</sub>	3.15	8,0	8,0	8,0	90	90	90	Favors at HT, low P/Nb; In-NbP
Orthorhombic Nb <sub>1.91</sub> P <sub>2.82</sub> O <sub>12</sub>	3,31	12.1	8,7	8,7	90	90	90	Minor phase in both NbP & In-NbP Favors at LT

# Indium doping

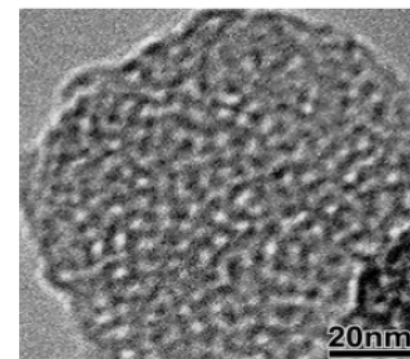
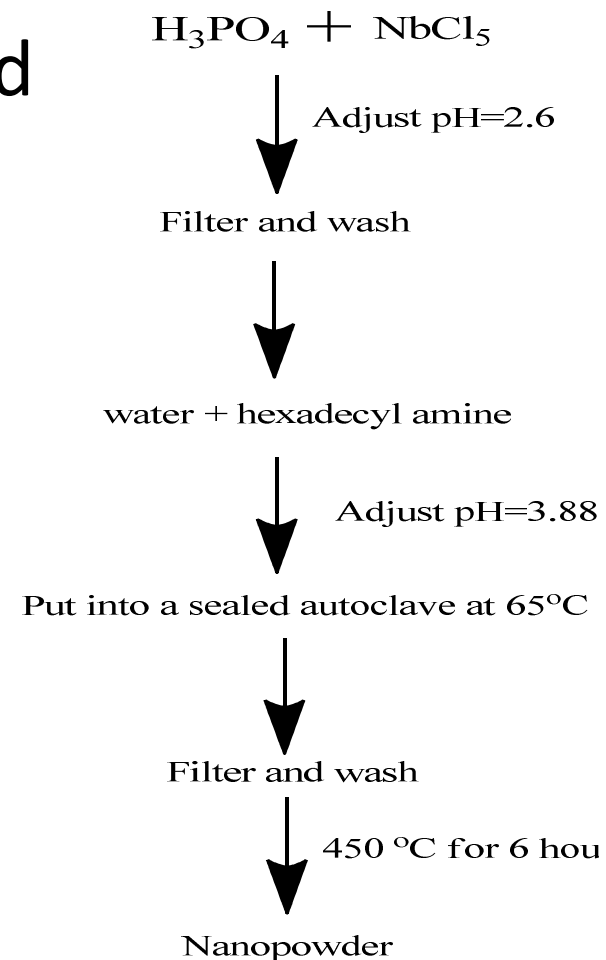
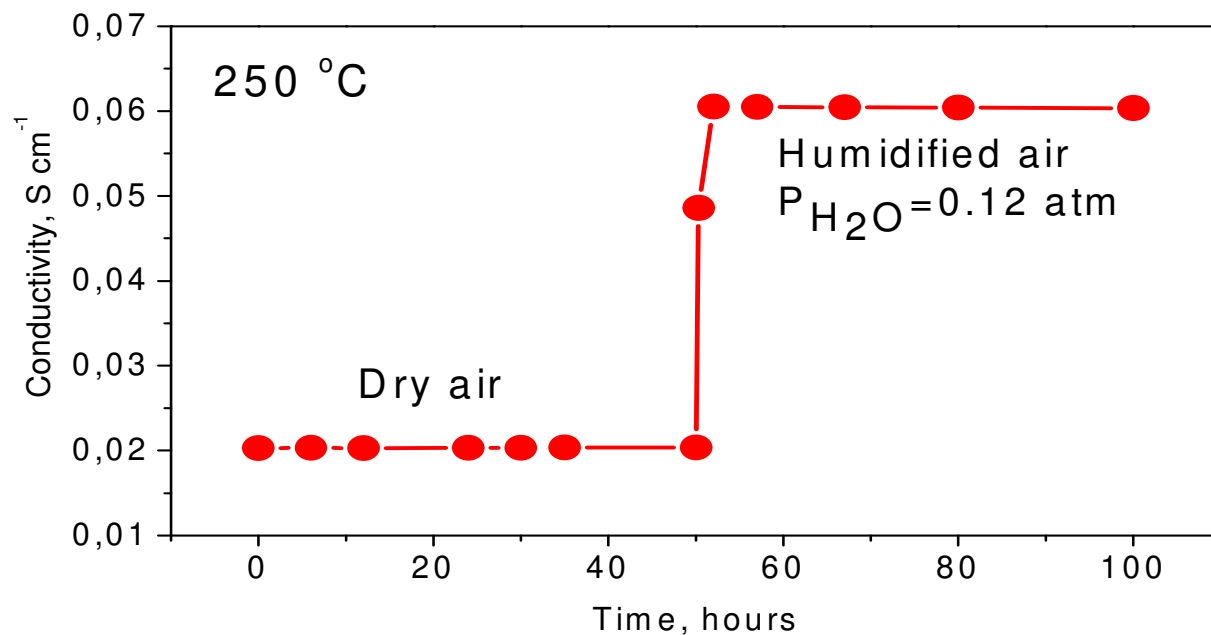
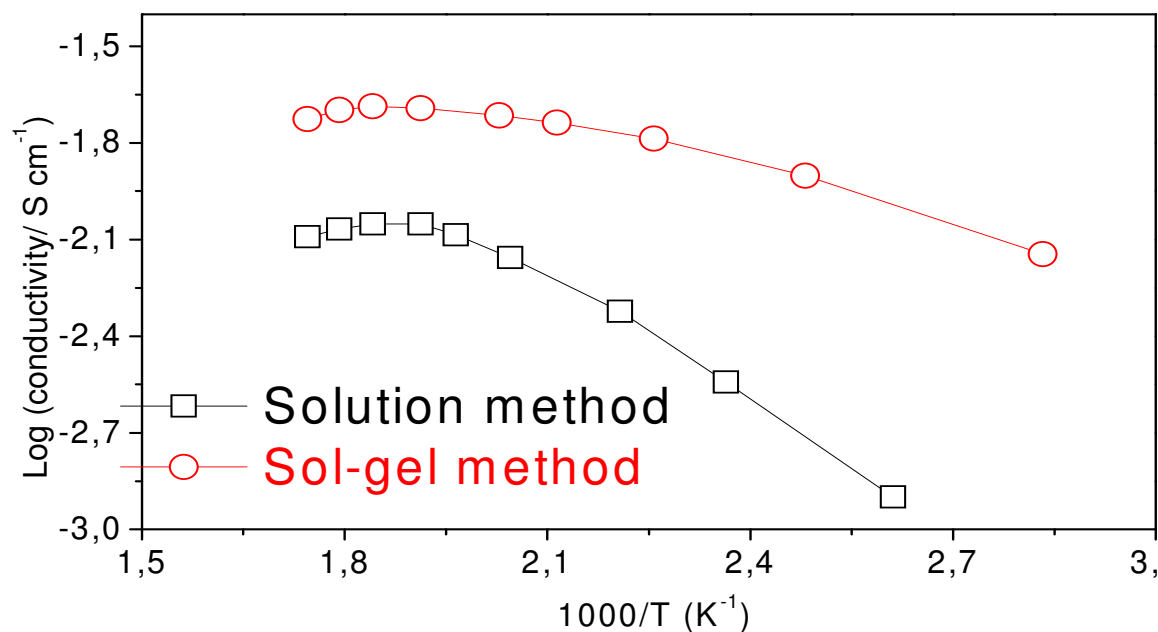
- anhydrous conductivity

- Cubic  $\text{Nb}_2\text{P}_4\text{O}_{15}$  favored
- OH groups enhanced/stabilized concentration & mobility



Un-humidified atmosphere  
250°C

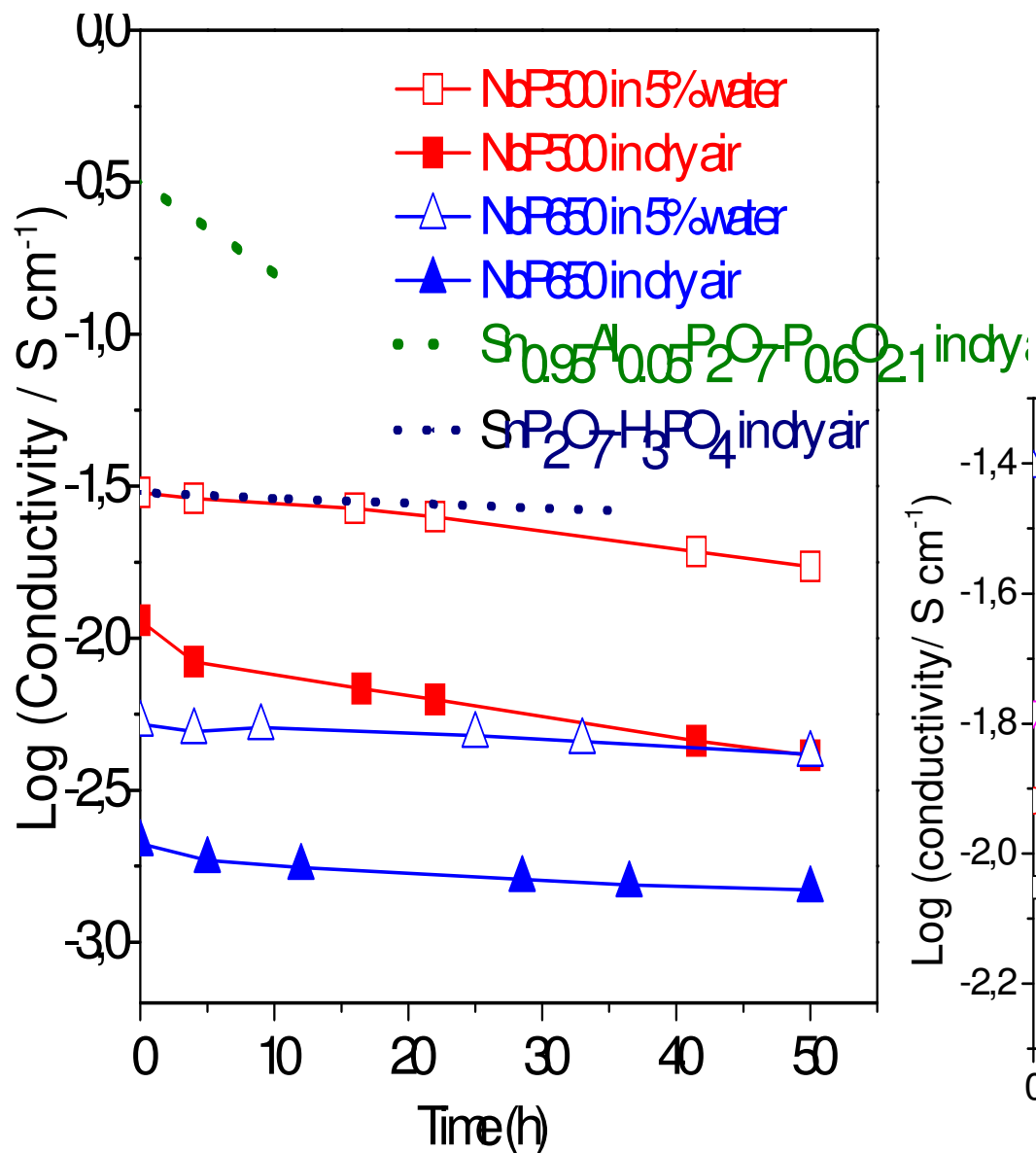
# Morphology effects - sol-gel method



BET: 480 m<sup>2</sup> g<sup>-1</sup>

# Heat Treatment Temperature

Under unhumidified atmosphere

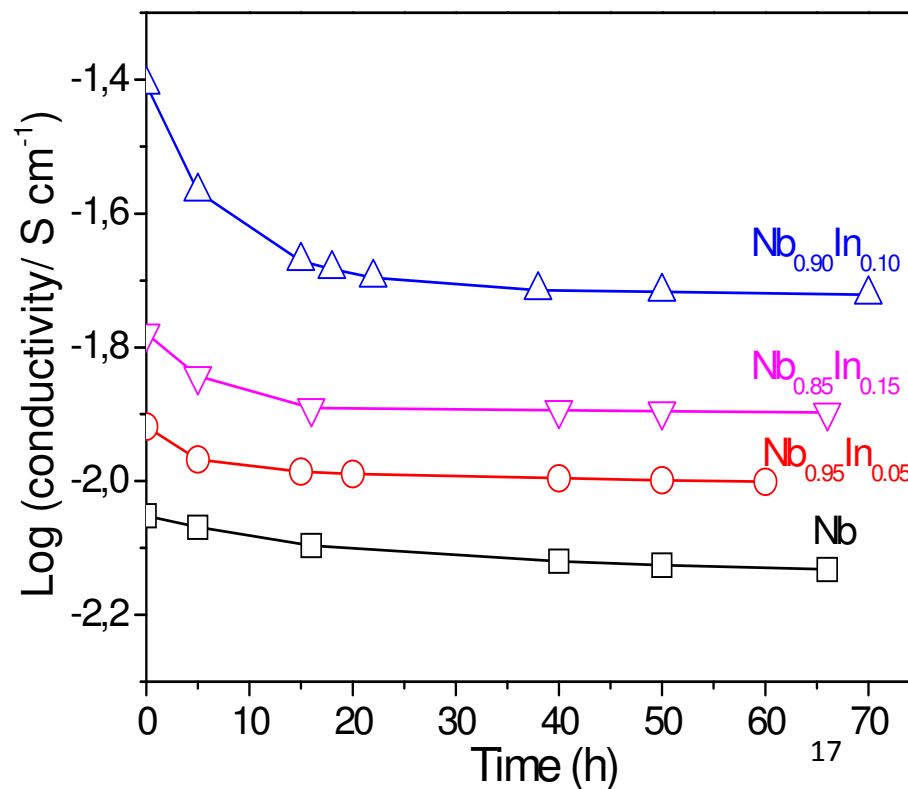


Heat treatment temperatures

- better stability for 650 °C

- improved stability  
at 5% water vapor

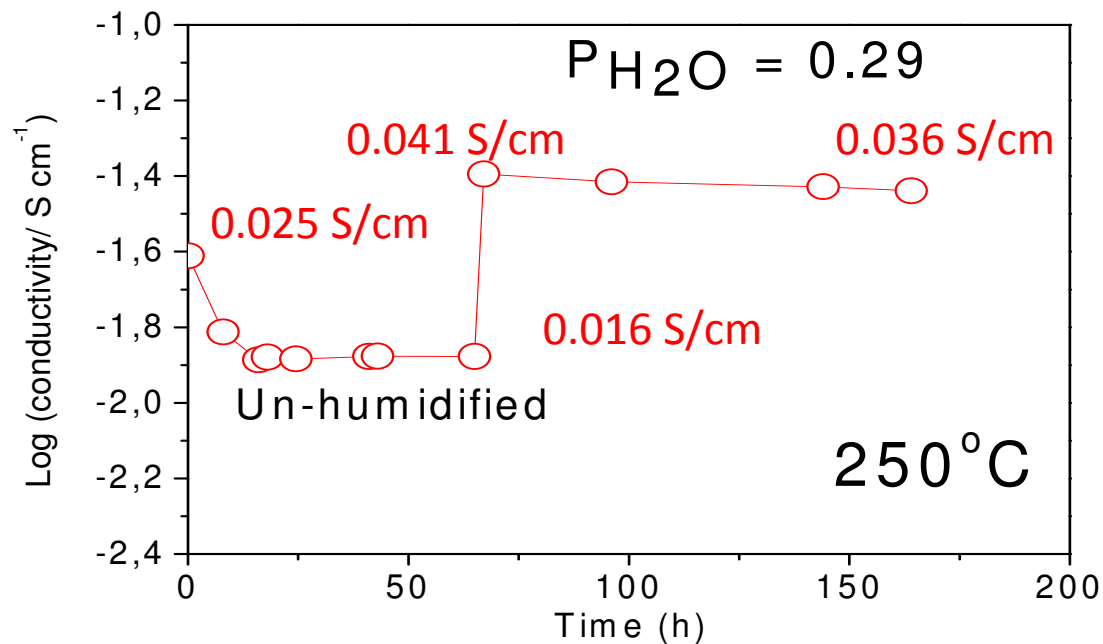
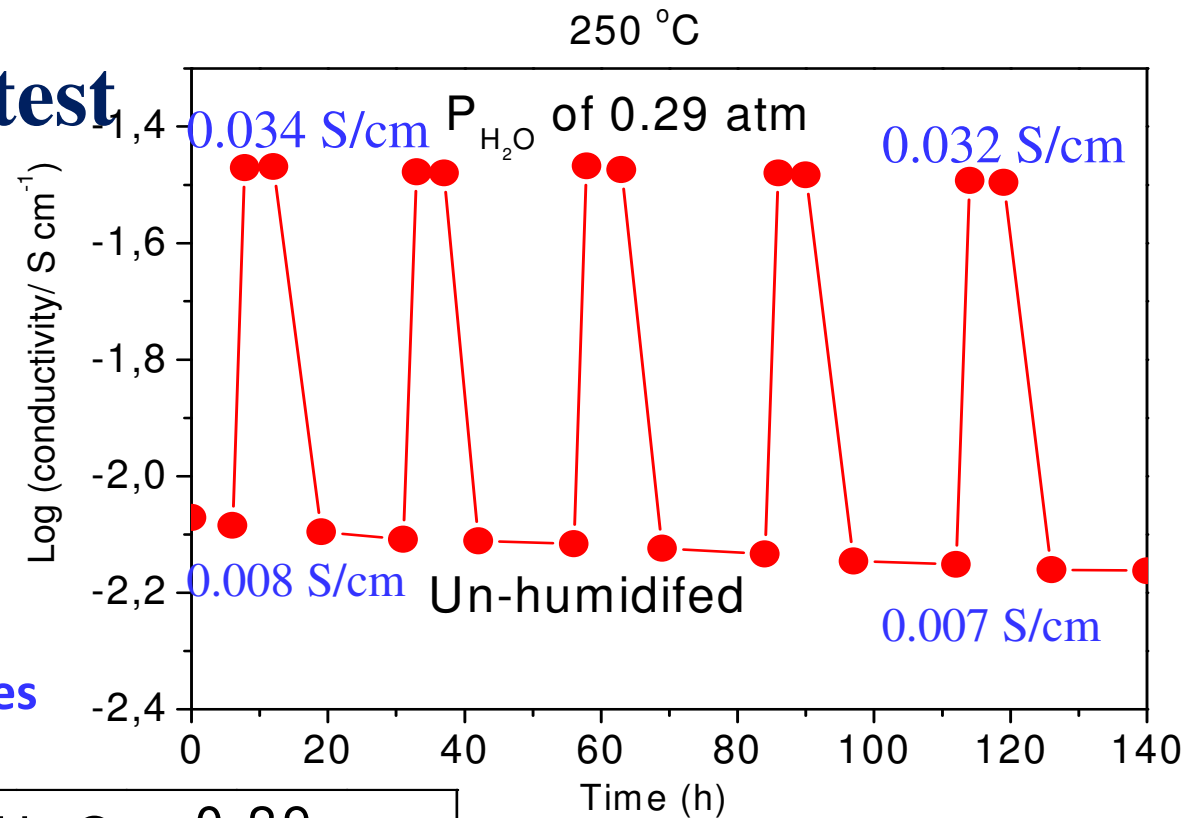
- similar for other phosphates ?





# Further stability test

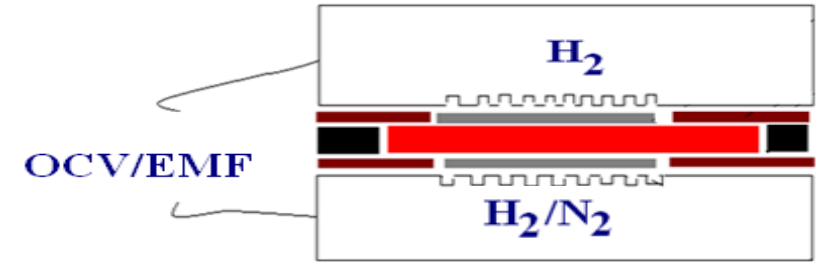
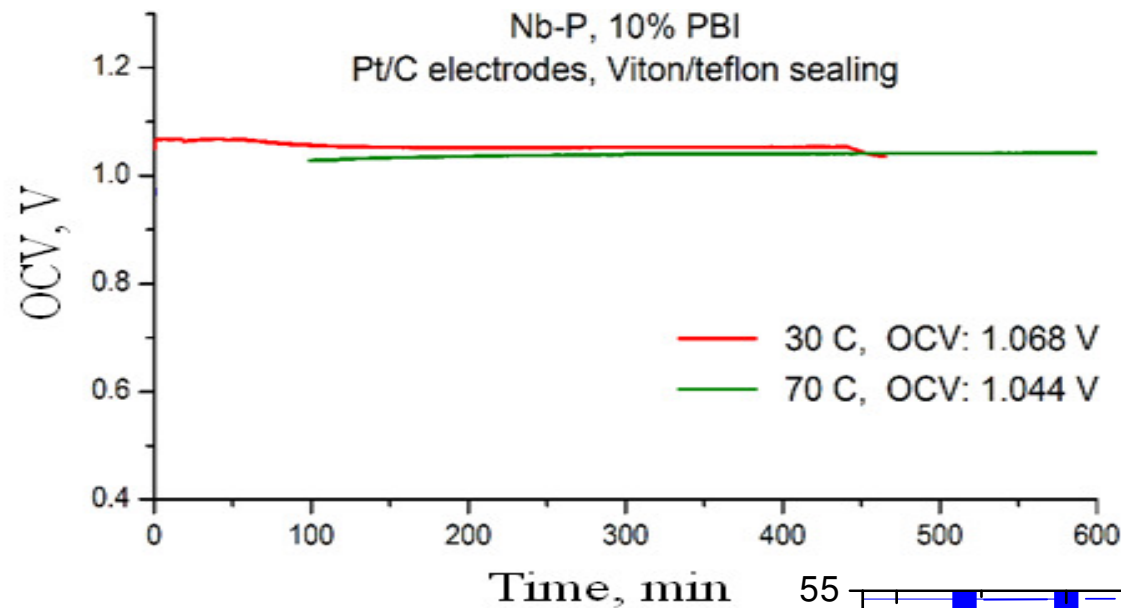
Under un-humidified  
and humidified atmospheres



## Daily humidity cycling

- $P_{H_2O} = 0 \rightarrow 0.29 \rightarrow 0$  atm
- Humidified period: 3 hrs

# OCV & EMF

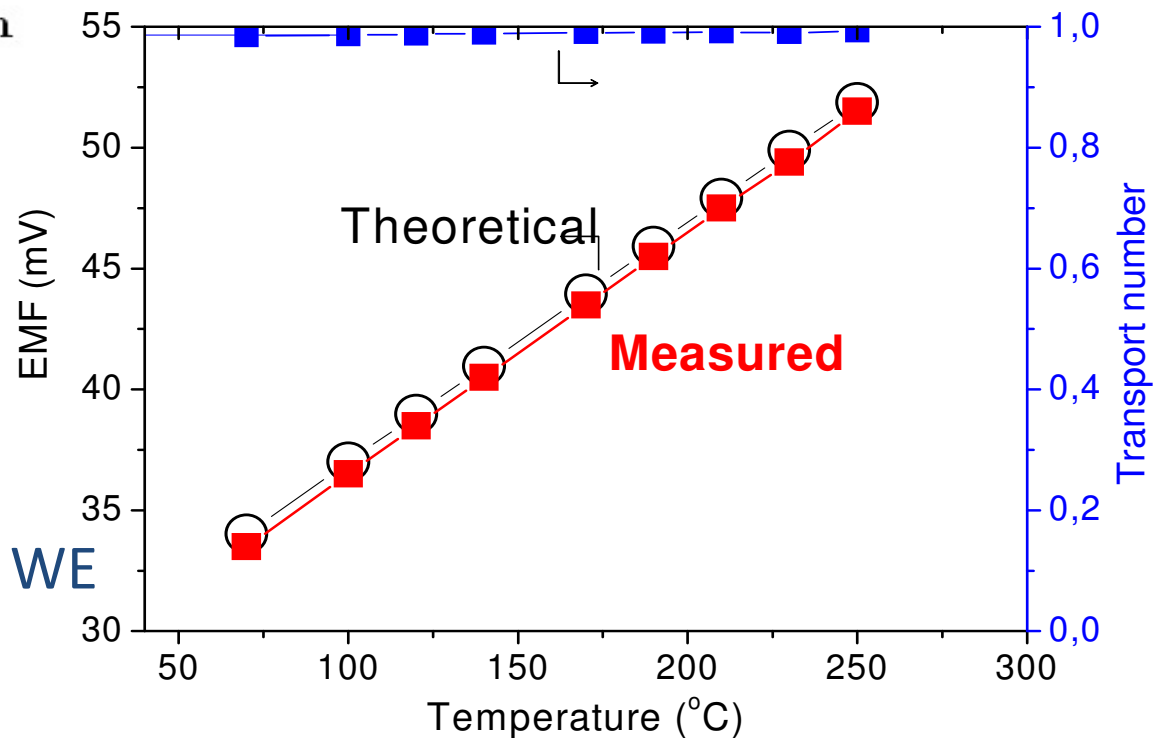


$$EMF = \frac{RT}{2F} \ln \left[ \frac{P_{H_2}^1}{P_{H_2}^2} \right]$$

Following well the Nerst equation,  
- indicating the conductivity protonic

$$\frac{P_{H_2}^1}{P_{H_2}^2} = 0.11$$

Efforts to assemble FC and WE  
cells are under the way.



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- Danish Agency for Science, Technology and Innovationan  
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- Danish Public Service Obligations (ForskEL programme)  
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